The exact Hohenberg-Kohn functional for a lattice model

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MAX-PLANCK-GESELLSCHAFT

Introduction

For a discretized soft-Coulomb lattice model we investigate the exact solution of the many-body Schrdinger equation in Fock space. Using quadratic optimization with quadratic constraints, or alternatively exact diagonalization, we explicitly construct the exact Hohenberg-Kohn functional and the mapping from densities to wavefunctions. We analyze the resulting exact Hohenberg-Kohn functional and draw conclusions for the construction of approximate functionals.

Two-site soft-Coulomb model

Hamiltonian

$$
\begin{aligned}
\hat{H} &= \hat{T} + \hat{W} + \hat{V} \\
\hat{T} &= -t_0 \sum_{l,\sigma} (\hat{c}^\dagger_{l,\sigma}\hat{c}_{l+1,\sigma} + \hat{c}^\dagger_{l+1,\sigma}\hat{c}_{l,\sigma}) + 2t_0 \sum_{l,\sigma} \hat{n}_{l,\sigma} \\
t_0 &= \frac{\hbar^2}{2m_e\Delta^2} \\
\hat{W} &= \sum_{l,m,\sigma,\sigma'} \frac{e^2 \hat{c}^\dagger_{l,\sigma}\hat{c}^\dagger_{m,\sigma'}\hat{c}_{m,\sigma'}\hat{c}_{l,\sigma}}{2\sqrt{(l\Delta - m\Delta)^2 + c}} \\
\hat{V} &= \sum_{l,\sigma} \hat{n}_{l\sigma} \cdot v_{l,\sigma}
\end{aligned}
$$

Density and spin operators

$$
\begin{aligned}
\hat{n} &= \sum_{j,\sigma} \hat{c}^\dagger_{j,\sigma}\hat{c}_{j,\sigma} \\
\hat{S}_x &= \frac{1}{2}\sum_j (\hat{c}^\dagger_{j\uparrow}\hat{c}_{j\downarrow} + \hat{c}^\dagger_{j\downarrow}\hat{c}_{j\uparrow}) \\
\hat{S}_y &= \frac{1}{2} i \sum_j (-\hat{c}^\dagger_{j\downarrow}\hat{c}_{j\uparrow} + \hat{c}^\dagger_{j\uparrow}\hat{c}_{j\downarrow}) \\
\hat{S}_z &= \frac{1}{2}\sum_j (\hat{n}_{j\uparrow} - \hat{n}_{j\downarrow}) \\
\hat{S}^2 &= \hat{S}^2_x + \hat{S}^2_y + \hat{S}^2_z
\end{aligned}
$$

We consider different particle numbers by including a chemical potential μ.

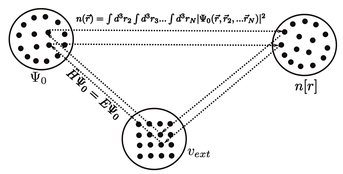
Levy-Lieb constraint search (M. Levy 1979 [1], E. Lieb 1983 [2])

Expand eigenfunctions in a complete basis set (energy eigenfunctions, Slater-Determinants, etc.)

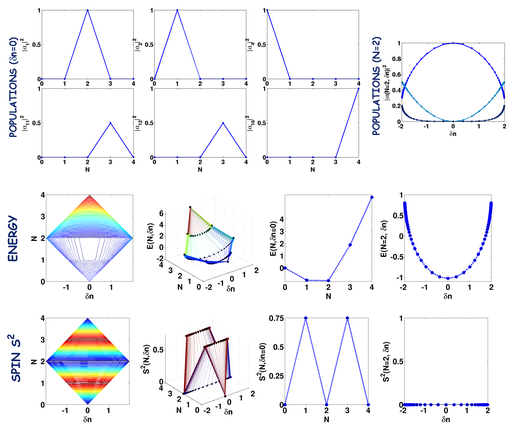
$$|\Psi[n]\rangle = \sum_{j=1}^{4^M} \alpha_j[n]\,|\,\phi_j\,\rangle\,,\ \text{M number of sites}$$

Hohenberg-Kohn functional

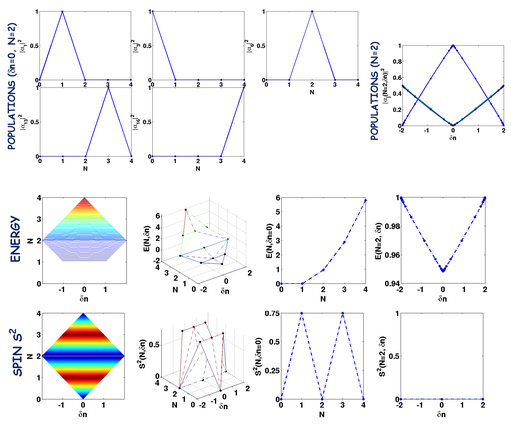
$$
\begin{aligned}
F_{\rm HK}(\alpha_1,...,\alpha_{4^M})[n] &= \min_{\Psi\to n} \langle\,\Psi[n]\,|\,\hat{T}+\hat{W}\,|\,\Psi[n]\,\rangle \\
&= \min_{\Psi\to n} \sum_{j,k=1}^{4^M} \alpha^*_j[n]\alpha_k[n]\,\langle\,\phi_j\,|\,\hat{T}+\hat{W}\,|\,\phi_k\,\rangle
\end{aligned}
$$



High-density limit (large hopping $t_0 = 1$)



Low-density limit (small hopping $t_0 = 0.001$)



Conclusion & Outlook

- The exact Hohenberg-Kohn functional shows a softened intra-system derivative discontinuity in the low-density limit.
- Similarly to the energy functional, also the populations as functional of the density show a softened intra-system derivative discontinuity.
- Expectation values of operators are affected by the softened intra-system dervative discontinuity of populations.

Soft-Coulomb molecules in 1D

Hamiltonian

$$
\begin{aligned}
\hat{H}(\alpha) &= \hat{T} + \hat{W} + \hat{V}(\alpha) \\
\hat{T} &= \sum_{j=1}^{2} -\frac{d^2}{dx_j^2} \\
\hat{W} &= \frac{1}{2}\sum_{i\neq j}^{2} \frac{1}{\sqrt{(x_i - x_j)^2 + 1}} \\
\hat{V}(\alpha) &= \sum_{j=1}^{2} \frac{Z_1(\alpha)}{\sqrt{(x_j - d)^2 + 1}} + \frac{Z_2(\alpha)}{\sqrt{(x_j + d)^2 + 1}}
\end{aligned}
$$

$Z_1(\alpha) = -\alpha, Z_2(\alpha) = -(2-\alpha),\ \alpha \in [0,2], \quad d = 3,8$ Bohr

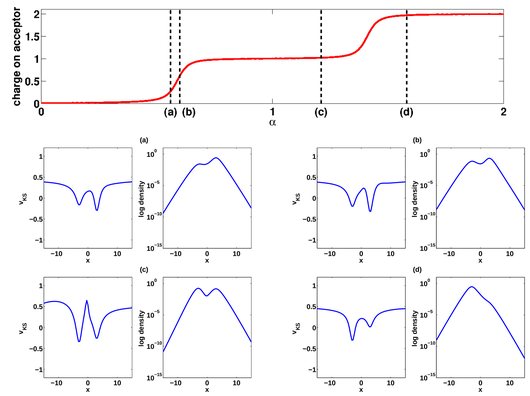
Exact Kohn-Sham potential for two electrons in spin singlet configuration (Helbig et al. 2009 [3])

$$v_{\rm KS}(x) = \frac{1}{2}\frac{\nabla^2\sqrt{n(x)}}{\sqrt{n(x)}} + \epsilon_1$$

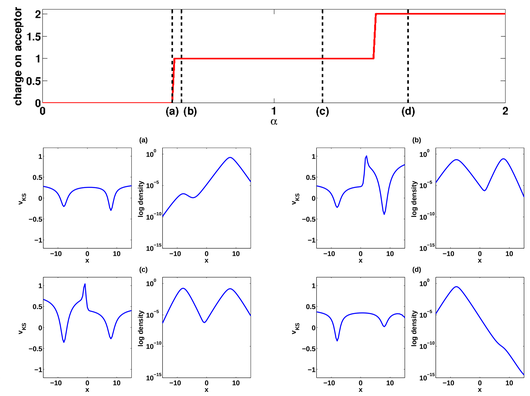
Exact solution of static two-electron Schrödinger equation with octopus (A. Castro et al. [4])

$$
\begin{aligned}
\hat{H}(\alpha)\Psi_j(\alpha) &= E_j(\alpha)\Psi_j(\alpha) \\
n(x) &= \langle\,\Psi\,|\,\hat{n}(x)\,|\,\Psi\,\rangle \\
\hat{n}(x) &= \sum_j \delta(x - x_j)
\end{aligned}
$$

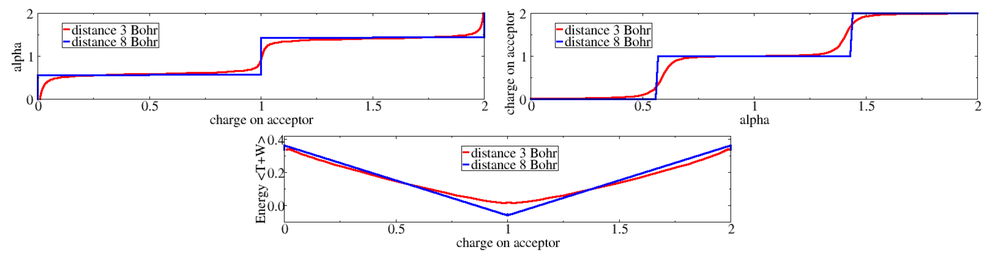
High-density limit (small distance $d = 3$ Bohr)



Low-density limit (large distance $d = 8$ Bohr)



Softened intra-system derivative discontinuity



Conclusion & Outlook

- We observe softened intra-system derivative discontinuity also for soft-Coulomb molecules in 1D.
- We currently develop an approximate functional which incorporates the intra-system derivative discontinuity.

References

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